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Synthesis and mesomorphic properties of fluoro and isothiocyanato biphenyl tolane liquid crystals

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Four series of high birefringence biphenyl tolane liquid crystals having a terminal isothiocyanato or fluoro group were synthesized; their mesomorphic properties were studied by optical polarizing microscopy and DSC. These biphenyl tolane compounds exhibit reasonably low melting points and high birefringence of 0.37–0.49. By using these compounds a eutectic mixture was formulated exhibiting a wide nematic range, high figure-of-merit and low viscosity.

1. Introduction

High birefringence (Δn) liquid crystals (LCs) are useful in super twisted nematic LC displays [1] polarizer-free reflective displays such as polymer-dispersed LCs [2], cholesterics [3], holographic switching devices [4], polarizers and directional reflectors [5, 6]. Apart from these display applications, these materials are also useful for laser beam steering using optical phased arrays and for spatial light modulators [7–9]. The Δn values of the LC materials are determined mainly by their electron conjugation, differential oscillator strength and order parameter [10].

To achieve high Δn , molecules that contain highly polar groups and high electron density, such as biphenyl rings or acetylene linking groups, are the preferred candidates. However, materials having high optical anisotropy may also possess high melting point and high viscosity which are detrimental to practical applications [11–21]. Several molecular structures with high Δn values, e.g. diphenyldiacetylene [22, 23], bistolane [17, 24, 25], naphthalene tolanes [26], and thiophenyldiacetylene [27, 28] have been widely studied. The Δn values of these compounds were reported in the range 0.4–0.6. Among them the diacetylene compounds do not have adequate UV and thermal stabilities, and thus their application is limited [29].

In this work, we report four series of highly birefringent tolane liquid crystals having a terminal isothiocyanato or fluoro group. Phenyl or biphenyl

rings linked by an ethynyl unit were used as the core structure [30]. The synthesized compounds were characterized by low melting point, relatively low viscosity, and high optical anisotropy, and some may be suitable for immediate practical applications.

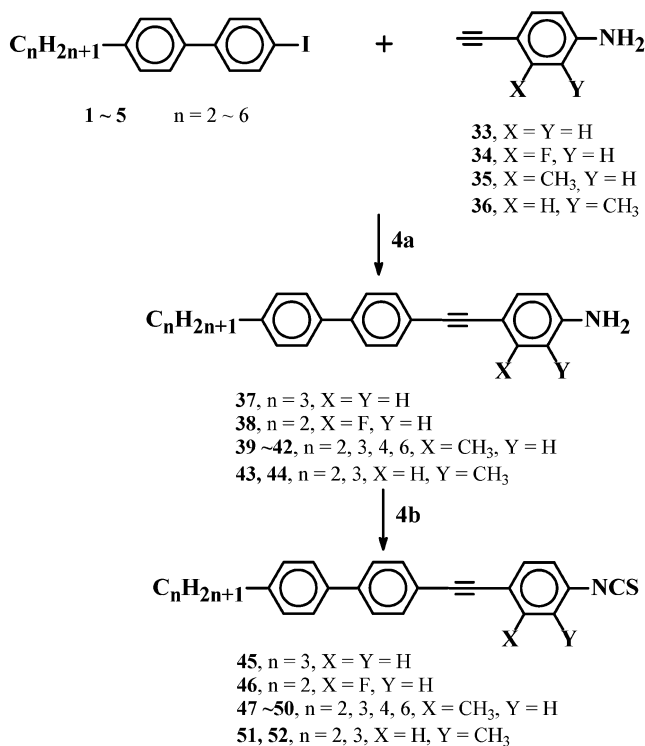
2. Experimental

2.1. Characterization techniques

^1H NMR spectra were measured with a Varian 300 MHz spectrometer. Infrared spectra were obtained by using a Perkin-Elmer Spectrum One spectrophotometer in the range 400–4000 cm^{-1} . Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Pyris Diamond DSC instrument at a heating rate of 10°C min^{-1} . A Carl-Zeiss Axiophot polarizing microscope equipped with a Mettler FP 82 hot stage and a Mettler FP 80 central processor was used to observe the mesomorphic textures. The molecular mass and elemental analysis results were obtained from a T-200 GC/MS spectrometer and Heraeus CHN-OS RAPID instrument, respectively.

For electro-optic measurements homogenous cells with cell gap $d \sim 8 \mu\text{m}$ were used. An a.c. voltage with 1 kHz square waves was used to drive the LC cell whose inner surfaces were coated with indium tin oxide (ITO) electrodes. On top of the ITO, the substrate was covered with a thin polyimide alignment film. The cell was placed on a heating/cooling stage with a temperature stability of 0.2°C. Commercial LCs ZLI-1565 and ZLI-1132 (Merck) were used as the host. A conventional

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4a ... PdCl₂(PPh₃)₂, PPh₃, CuI, TEA.

4b ... Thiophosgene, CHCl₃, CaCO₃.

Scheme 4. Synthesis of compounds 45–52.

and the mixture stirred at 60°C for 24 h. After cooling to room temperature, the mixture was filtered and the filtrate concentrated *in vacuo* to remove triethylamine. The crude product was dissolved in diethyl ether and extracted with aqueous ammonium chloride solution. The organic phase was then washed with saturated aqueous NaCl and dried over MgSO₄. The crude product isolated by evaporating the solvent was purified by column chromatography using ethyl acetate/*n*-hexane=1/10 as eluant to give a white solid; yield 1.20 g (80%). ¹H NMR (CDCl₃): δ 1.21–1.26 (t, 3H), 2.62–2.69 (q, 2H), 7.09–7.69 (m, 12H). ¹³C NMR (CDCl₃): δ 15.3, 28.8, 88.5, 90.4, 115.6, 115.9, 120.3, 122.4, 126.8, 128.0, 128.4, 128.5, 128.6, 131.6, 132.0, 133.0, 139.7, 144.8, 161.0, 164.2. IR (KBr) ν_{\max} (cm⁻¹): 2969, 2932, 2866, 2251, 1594, 1510, 1457, 1071, 833. MS *m/z* 300 (M⁺), 285. Anal: calc. for C₂₂H₁₇F, C 87.97, H 5.70; found, C 87.74, H 5.81%.

2.2.3. 1-(4-Propylbiphenyl)-2-(4-amino-2-methylphenyl) acetylene, 40. Compound 2 (1.61 g, 5 mmol), Pd(PPh₃)₂Cl₂ (0.07 g, 0.1 mmol), triphenylphosphine (0.1 g, 0.4 mmol), CuI (0.04 g, 0.2 mmol) and dry triethylamine (100 ml) were mixed and stirred at room temperature for 30 min under nitrogen. A solution of

compound 35 (0.72 g, 5.5 mmol) dissolved in 50 ml of triethylamine was added dropwise and the mixture stirred at 70°C for 24 h. After cooling to room temperature, the mixture was filtered and filtrate concentrated *in vacuo* to remove triethylamine. The crude product was dissolved in diethyl ether and extracted with aqueous ammonium chloride solution. The organic phase was then washed with saturated aqueous NaCl and dried over MgSO₄. The crude product isolated by evaporating the solvent was purified by column chromatography using ethyl acetate/*n*-hexane=1/4 as eluant to give a yellow solid; yield 1.05 g (64%). ¹H NMR (δ, CDCl₃): 0.96–0.98 (t, 3H), 1.65–1.69 (m, 2H), 2.45 (s, 3H), 2.60–2.66 (q, 2H), 6.50 (s, 2H), 7.00–7.57 (m, 11H), IR (KBr) ν_{\max} (cm⁻¹): 3561, 3388, 2960, 2943, 2860, 1630, 1490, 1400, 1110, 1003, 823.

2.2.4. 1-(4-Propylbiphenyl)-2-(4-isothiocyanato-2-methylphenyl)acetylene, 48. Compound 40 (1.0 g, 3.1 mmol) was dissolved in 15 ml of chloroform and the solution added to a stirred, cooled (0°C) mixture of water (10 ml) calcium carbonate (0.46 g, 4.6 mmol), chloroform (8 ml) and thiophosgene (0.39 g, 4.0 mmol), then stirred at 0°C for 4 h. The stirred mixture was allowed to come to room temp, then heated to 45°C and held for 20 min before pouring into water. The aqueous layer was washed with dichloromethane and the combined organic extracts were washed with 1% aqueous HCl, water, brine and then dried (MgSO₄). The crude product isolated by evaporating the solvent was purified by column chromatography using ethyl acetate/*n*-hexane=1/10 as eluant to give a white solid; yield 0.91 g (80%). ¹H NMR (δ, CDCl₃): 0.93–0.98 (t, 3H), 1.63–1.70 (m, 2H), 2.49 (s, 3H), 2.59–2.64 (q, 2H), 7.00–7.57 (m, 11H). ¹³C NMR (δ, CDCl₃): 13.8, 20.6, 24.5, 37.7, 87.8, 95.2, 121.5, 122.4, 123.0, 126.4, 126.6, 126.7, 126.8, 127.0, 128.9, 129.0, 130.5, 131.8, 131.9, 132.8, 136.0, 137.5, 141.3, 141.9, 142.5. IR (KBr) ν_{\max} (cm⁻¹): 2954, 2923, 2863, 2215, 2040, 1634, 1498, 1464, 1382, 1003, 823. MS *m/z* 367 (M⁺), 338. Anal: calc. for C₂₅H₂₁NS, C 81.71, H 5.76, N 3.81; found, C 81.53, H 5.77, N 3.98%.

3. Results and discussion

3.1. Thermal transitions and mesomorphic properties

The chemical structure, phase transition temperatures, associated enthalpies and optical anisotropy values for the reported novel compounds and some known materials for comparison are shown in tables 1–5.

Table 2 summarizes the phase transitions of compounds 9–17. They all exhibit an enantiotropic nematic

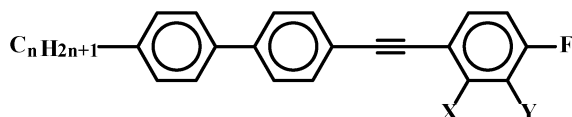
Table 1. Purity and elemental analysis data for some representative bistolanes.

Cpd. No.	Purity/%	Elemental analysis, found (calc.)/%		
		C	H	N
9	99.1%	87.83(87.97)	5.85(5.70)	—
10	99.2%	87.78(87.87)	6.14(6.09)	—
11	98.4%	87.42(87.77)	6.68(6.44)	—
12	98.8%	87.88(87.68)	6.49(6.77)	—
13	98.5%	87.61(87.87)	6.21(6.09)	—
14	99.3%	87.70(87.77)	6.51(6.44)	—
15	99.0%	87.53(87.69)	6.55(6.76)	—
16	99.2%	87.55(87.60)	7.14(7.07)	—
17	98.8%	87.94(87.77)	6.76(6.44)	—
24	99.0%	87.74(87.97)	5.81(5.70)	—
25	98.5%	87.53(87.87)	6.17(6.09)	—
26	98.4%	87.48(87.77)	6.62(6.44)	—
27	99.0%	87.54(87.68)	6.90(6.77)	—
28	98.4%	87.72(87.97)	7.13(5.70)	—
30	99.3%	92.26(92.21)	7.59(7.74)	—
31	99.0%	91.75(91.99)	8.21(8.01)	—
32	99.0%	91.63(91.75)	8.52(8.75)	—
45	99.2%	81.42(81.55)	5.70(5.42)	3.98(3.96)
46	99.0%	77.45(77.29)	4.33(4.51)	3.97(3.92)
47	98.6%	81.17(81.55)	5.68(5.42)	4.27(3.96)
48	99.0%	81.53(81.71)	5.77(5.76)	3.81(3.92)
49	98.4%	81.56(81.85)	6.25(6.08)	3.77(3.67)
50	99.1%	81.93(82.11)	6.63(6.64)	3.45(3.42)
51	99.0%	81.41(81.55)	5.33(5.42)	4.11(3.96)
52	99.0%	81.90(81.71)	5.51(5.76)	4.02(3.81)

phase. Compounds **9–12** contain the same terminal fluoro group on the phenyl ring and different alkyl chain lengths on the biphenyl ring. Their phase

transitions are plotted against the carbon number of the alkyl chain in figure 1. It can be seen that both melting and clearing points show an odd–even effect

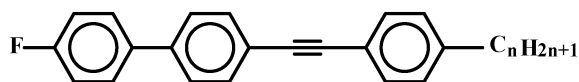
Table 2. Phase transition temperatures and corresponding enthalpy changes of the fluorinated biphenyl tolans: Cr=crystal, S=smectic, N=nematic, I=isotropic.



Cpd. No.	<i>n</i>	<i>X</i>	<i>Y</i>	Phase transition temperature/°C and enthalpy change/kcal/mol <small>heating scan cooling scan</small>
9	2	H	H	Cr 130.7(6.39) SmX 133.1(–) ^a N 136.2(0.14) I I 134.1(0.13) N 124.4(2.77) SmX 84.0(3.35) Cr
10	3	H	H	Cr 185.7(3.41) N 212.9(0.20) I I 209.7(0.28) N 179.7(3.44) Cr
11	4	H	H	Cr 172.5(3.27) N 183.3(0.12) I I 176.5(0.18) N 164.2(3.40) Cr
12	5	H	H	Cr 178.6(3.01) SmX 183.8(–) ^a N 199.2(0.13) I I 93.5(0.27) N 179.0(–) ^a SmX 173.8(3.13) Cr
13	2	CH ₃	H	Cr 130.0(5.68) N 169.2(0.12) I I 165.9(0.11) N 98.1(3.47) Cr
14	3	CH ₃	H	Cr 102.6(4.99) N 172.9(0.18) I I 169.9(0.17) N 102.4(0.17) SmA 83.5(1.02) SmX 58.3(2.87) Cr
15	4	CH ₃	H	Cr 84.8(4.94) SmA 98.4(0.20) N 149.5(0.16) I I 147.5(0.15) N 96.3(0.23) SmA 81.3(4.34) Cr
16	5	CH ₃	H	Cr 84.9(5.19) SmA 126.4(0.23) N 166.5(0.13) I I 164.1(0.19) N 123.8(0.26) SmA 81.2(5.20) Cr
17	3	H	CH ₃	Cr 117.1(2.45) SmX 140.3(2.05) N 148.8(0.07) I I 142.7(0.16) N 131.8(2.26) SmX 57.5(2.06) Cr

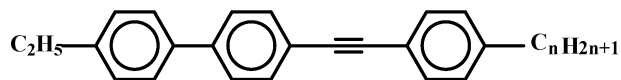
^aOverlapped transition.

Table 3. Phase transition temperatures and corresponding enthalpy changes of the 4-fluorophenyl-4'-alkyl tolanes: Cr=crystal, S=smectic, N=nematic, I=isotropic.



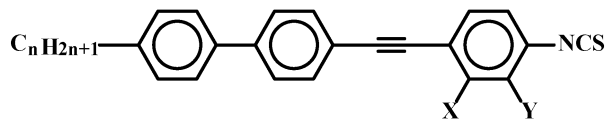
Cpd. No.	<i>n</i>	Phase transition temperature/°C and enthalpy change/kcal/mol <small>heating scan cooling scan</small>
24	2	Cr 173.0(4.36) I I 143.0(4.14) Cr
25	3	Cr 174.3(3.66) N 210.9(0.14) I I 206.5(0.16) N 170.2(2.68) Cr
26	4	Cr 169.9(2.63) N 188.7(0.11) I I 182.5(0.14) N 163.6(2.71) Cr
27	5	Cr 176.6(2.72) N 203.8(0.16) I I 199.9(0.22) N 170.9(2.99) Cr
28	6	Cr 174.9(2.58) N 188.6(0.15) I I 186.0(0.2) N 171.0(3.19) Cr

Table 4. Phase transition temperature and corresponding enthalpy changes of dialkyl-substituted biphenyl tolanes: Cr=crystal, S=smectic, N=nematic, I=isotropic.



Cpd. No.	<i>n</i>	Phase transition temperature/°C and enthalpy change/kcal/mol <small>heating scan cooling scan</small>
29	3	Cr 147.8(3.25) N 209.2(0.18) I I 205.4(0.37) N 141.3(3.26) Cr
30	4	Cr 141.0(3.3) N 203.0(0.19) I I 199.0(0.35) N 134.0(3.29) Cr
31	5	Cr 137.7(2.17) N 200.7(0.21) I I 196.0(0.15) N 131.2(2.16) Cr
32	6	Cr 130.2(3.22) N 195.4(0.24) I I 190.4(0.34) N 124.4(3.34) Cr

Table 5. Phase transition temperature and corresponding enthalpy changes of the isothiocyanato biphenyl tolanes: Cr=crystal, S=smectic, N=nematic, I=isotropic.



Cpd. No.	<i>n</i>	<i>X</i>	<i>Y</i>	Phase transition temperature/°C and enthalpy change/kcal/mol <small>heating scan cooling scan</small>
45	3	H	H	Cr 200.0(5.32) SmA 209.0(0.35) N 266.0(0.06) I I 261.5(0.06) N 184(0.31) SmA 136.2(4.70) Cr
46	2	F	H	Cr 146.9(6.86) N 247.9(0.24) I I 243.1(0.13) N 137.7(3.64) Cr
47	2	CH ₃	H	Cr 152.0(5.75) N 201.4(0.06) I I 196.7(0.06) N 122.0(4.67) Cr
48	3	CH ₃	H	Cr 117.2(5.35) N 188.1(0.18) I I 181.4(0.10) N 104.2(4.89) Cr
49	4	CH ₃	H	Cr 107.1(6.36) N 194.6(0.21) I I 192.6(0.13) N 67.6(4.89) Cr
50	5	CH ₃	H	Cr 82.5(6.75) SmC 147.5(0.23) N 208.4(0.81) I I 205.9(0.16) N 145.8(0.21) SmC 78.5(5.84) Cr
51	2	H	CH ₃	Cr 137.0(4.76) SmA 151.9(0.19) N 214.5(0.23) I I 212.9(0.27) N 150.0(0.19) SmA 119.0(-) ^a SmX 115.1(4.22) Cr
52	3	H	CH ₃	Cr 147.5(7.01) N 207.7(0.24) I I 205.8(0.23) N 135.8(-) ^a SmX 133.1(5.41) Cr

^aOverlapped transition.

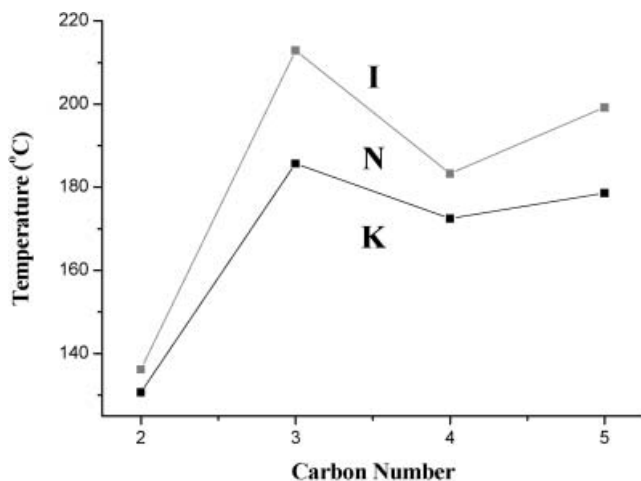


Figure 1. Dependence of transition temperature on the number of terminal group carbon atoms for compounds 9–12.

with increasing carbon number. Compounds 9 and 12 show an ordered smectic phase which can not be identified by optical microscopy. Compounds 13–16 contain similar structures to those of compounds 9–12, with an additional lateral methyl group at the C-2 position of the phenyl ring. Their phase transition temperatures are plotted against the carbon number of the alkyl chain in figure 2. In this case the clearing points show an odd–even effect with increasing carbon number, while melting temperatures decrease gradually. Compared with compounds 9–12, both melting and clearing points decreased on introducing a lateral methyl group. This is reasonable since the lateral group can hinder effective molecular packing and thus decrease transition temperatures. An exception was found for compound 13 which shows a similar clearing

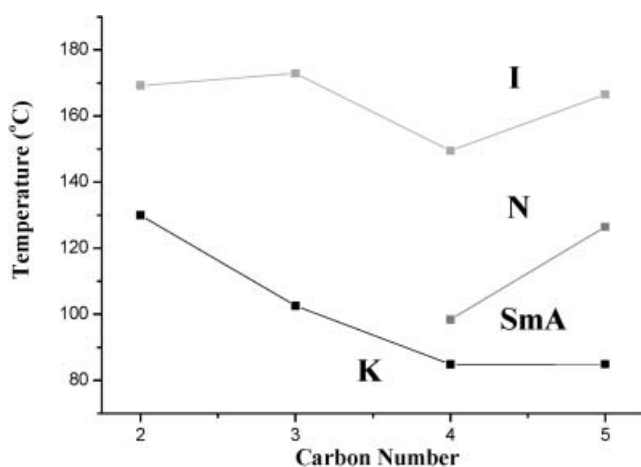


Figure 2. Dependence of transition temperature on the number of terminal group carbon atoms for compounds 13–16.

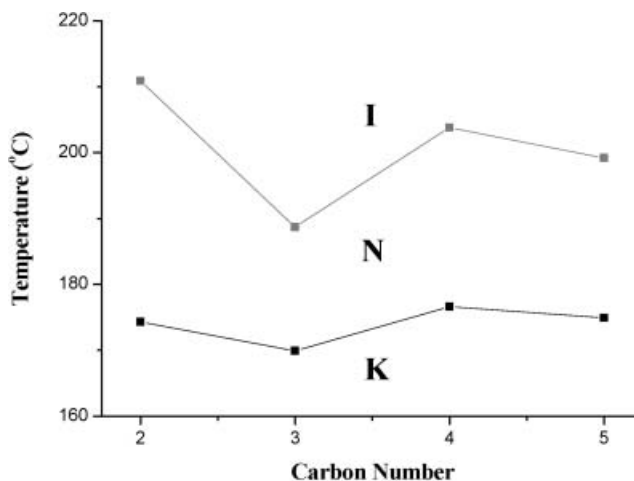


Figure 3. Dependence of transition temperature on the number of terminal group carbon atoms for compounds 25–28.

point to compound 9. The reason could be due to their short ethyl group. Both compounds 15 and 16 reveal an enantiotropic smectic A phase in addition to the nematic phase.

For comparison purposes, we synthesized compound 17 which contains a lateral methyl group at the C-3 position of the phenyl ring. Its melting and clearing points are lower than those of compound 10. Nevertheless, in comparison with compound 14, its melting point is higher but clearing point is lower.

Table 3 lists the phase transition temperatures of compounds 24–28. Compound 24 shows no mesomorphic properties, which may be due to the short ethyl group. Compounds 25–28 exhibit an enantiotropic nematic phase; their phase transition temperatures are plotted against the carbon number in figure 3. Both melting and clearing points show an odd–even effect with increasing carbon number. Comparing the chemical structures of this series of compounds with those of compounds 9–12, the difference is the locations of the fluoro and alkyl terminal groups which are reversed in both cases. The mesomorphic behaviour of the two series of compounds is very different. For example, compound 9 exhibits enantiotropic nematic and smectic phases while compound 24 shows no mesophase.

Table 4 summarizes the properties of the asymmetric dialkyl-substituted biphenyl tolans 29–32. In this series an ethyl group was placed on the biphenyl ring and, on the other side, different alkyl chains were introduced on the phenyl ring. They show enantiotropic mesomorphic behaviour, and only a nematic phase is observed. Their phase transition temperatures are plotted against the carbon number in figure 4. Both melting and clearing temperatures are decreased slightly with increasing

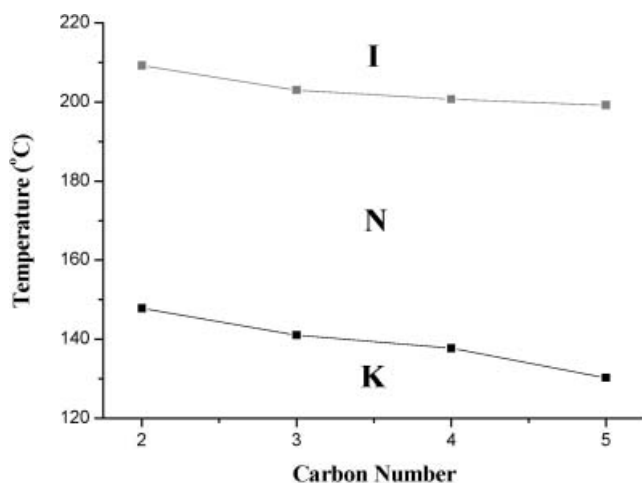


Figure 4. Dependence of transition temperature on the number of terminal group carbon atoms for compounds 29–32.

carbon number. This series of biphenyl tolanes shows much lower melting points than the fluorinated biphenyl tolanes 9–12 and 25–28.

Table 5 summarizes the phase transition temperatures of the isothiocyanato biphenyl tolanes 45–52. The chemical structures of these compounds are similar to those of compounds 9–17, with replacement of the terminal group by an isothiocyanato group. Compound 45 shows the highest transition temperature because of its linear structure without lateral substituents. As in

the introduction of a lateral methyl or fluoro group in compounds 46–52, the melting and clearing points are both decreased. In comparing compounds 46 and 47, the nematic range is increased on replacing the methyl with a fluoro group. Turning to compounds 47–50, the melting points are decreased with increasing alkyl chain length. Compounds 51 and 52 contain a lateral methyl group at the C-3 position of the phenyl ring. Both exhibit smectic phases in addition to a nematic phase, while their corresponding compounds 47 and 48 show only a nematic phase. Furthermore, both 51 and 52 exhibit much higher clearing points. On comparing the phase transition temperatures of isothiocyanato biphenyl tolanes 47–50 with those of the corresponding fluorinated biphenyl tolanes 13–16, it is seen that the isothiocyanato compounds show much higher melting and clearing points.

3.2. Optical anisotropy

The Δn value, defined as the difference between the two principal refractive indices of a uniaxial material, was estimated by the guest–host method. The Δn value of a guest–host system can be approximated from the equation:

$$(\Delta n)_{gh} = x(\Delta n)_g + (1-x)(\Delta n)_h. \quad (1)$$

In equation (1), the subscripts g, h, and gh denote guest, host, and guest–host cells, respectively, and x is the concentration (in wt%) of the guest compound. By

Table 6. Values of Δn for single compounds^a.

Cpd. No.	Compound structure	Δn
10		0.36
14		0.35
25		0.37
46		0.49 ^b
47		0.48 ^b
51		0.45*

^aData calculated from the guest–host systems using host mixture ZLI-1565: Cr–20.0 N 85.0 I (°C), $\Delta n=0.12$ at $T=23.5^\circ\text{C}$

^bHost mixture ZLI-1132 was used.

comparing the measured results for the guest–host mixtures with those of the host mixture, the Δn values of the guest compounds can be extrapolated.

The Δn values of some of the synthesized compounds are listed in table 6. Commercial LCs ZLI-1132 or ZLI-1565 were used as host mixture. It can be seen that Δn values of these compounds are in the range 0.35–0.49. For those compounds with a terminal isothiocyanato group, the Δn value is higher than that of the corresponding fluoro compounds. This is because the isothiocyanato group has an elongated electron conjugation than the fluoro group. On comparing compounds **10** and **14**, the Δn value was slightly decreased on introducing a lateral methyl group at the C-2 position. Compound **46** has the highest Δn of 0.49 and is expected to be useful for PDLC, cholesteric display, and laser beam steering applications.

4. Conclusions

Four series of novel high birefringence biphenyl liquid crystals with a terminal isothiocyanato or fluoro group were synthesized. A lateral methyl or fluoro group was introduced to modify their LC properties. Some of these compounds exhibit an odd–even effect in phase transition temperatures. The Δn value was determined by the guest–host method using a commercial LC as host matrix. Compounds containing both biphenyl and isothiocyanato moieties have a high Δn value. Compound **46** has the highest Δn of 0.49, and may be a good candidate for many display applications.

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